Chapter 24

Herbicides — A Double Edged Sword

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Additional information is available at the end of the chapter

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1. Introduction

Weeds represent a global agronomic problem that threatens the productivity of cultivated crops. Weeds compete with cultivated crops for the available moisture, nutrients and light. Consequently, weeds significantly reduce either crop yield or quality. Control of weeds is essential to maintaining the production of economic crops. Weed control may be achieved either through manual eradication or herbicide application. Balanced usage of herbicides should be considered in controlling weeds. Low concentrations of herbicides may act as growth regulators for the main crop metabolism [1]. However, in some cases, herbicides may affect the main crop adversely by interfering with its essential biochemical processes such as respiration, photosynthesis, protein metabolism, and hydrolytic enzyme activity [1].

Herbicide interference with the morphology, physiology and biochemical pathways of treated plants varies according to the characteristic actions of the herbicide and depends upon the degree of tolerance or susceptibility of the crop plant species. Environmental factors and soil conditions affecting plant growth, as well as herbicide formulation, herbicide degradation and application method would significantly influence the effects of herbicides on treated plants. Once an herbicide reaches the site of action in the treated plants, the biochemical processes are affected. Herbicides differ in their site of action and may have more than one site of action. As the herbicide concentration increases in plant tissue, additional sites of action may become involved. The effect of herbicides on growth, productivity and different metabolic activities has been studied extensively in many investigations such as in **El-Hadary** [1].

1.1. A word from the authors

Authors intended to give some examples for commercial herbicides that were applied in agronomic systems within the past fifty years. These examples include those herbicides which may now be internationally prohibited but are still used in the developing and under-

developing countries due to their low price and the little information available about them. References have been included that cover a long era of research concerning herbicide application in order to include those prohibited herbicides. Also, references were included that focus on research that was conducted in under- and developing countries.

1.2. Herbicides

This chapter will discuss different herbicide groups, classification, selectivity, interference with metabolic processes and hazardous action upon crop plants. Also, the relation to naturally occurring phenomena, such allelopathy and future prospects of genetic engineering in the production of plant herbicides themselves, will be mentioned.

2. Classification of herbicides (Broad lines)

There are different broad lines upon which herbicides could be classified:

2.1. Application timing

Time of application of an herbicide is so critical for getting satisfying results. Herbicides application is achieved either pre-emergence or post-emergence of the weed seedlings. Pre-emergence involves herbicide application prior to seed germination while post-emergence means application after seed germination and active growth. Moreover, post-directed application refers to targeting the treatment to a particular portion of the plant once emerged and growing.

2.2. Application method

Herbicides may be applied either as a foliar spray or a soil treatment. The application method may take either the broadcast pattern through treatment of the entire area or the spot pattern through specified area treatment.

2.3. Chemical groups

The chemical group to which an herbicide belongs indicates its mode of action. A good classification and description for herbicides is provided by "Compendium of Pesticide Common Names" at the web site of *http*://www.alanwood.net/pesticides/class_herbicides.html.

2.4. Mode of action

Herbicides poisonous action goes either by contact or systematically. Herbicides can be classified according to their mode of action into two categories; non-selective herbicides and selective herbicides. Non-selective herbicides are characterized by having a general poisonous effect to the plant cells while selective herbicides can recognize the plant which they affect and kill it by interference with its principle biochemical processes.

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3. Selectivity of herbicides

Selectivity of herbicides for eradicating weeds can be achieved through employing some factors related to:

3.1. Biochemical differences

Based on the biochemical differences between weeds and crops, or even weeds between each other, selectivity can be achieved. There is a great diversity of types of weeds usually growing in one crop. When employing an herbicide based on biochemical differences, the crop plant would possess a defense mechanism that is usually absent in most of the competing weed species. Consequently, the herbicide would react with the biochemical metabolism of the weeds without any fatal interference on main crop metabolism.

3.2. Morphological differences

The selectivity which depends upon morphological differences is characteristic for post-emergence herbicides. Dicotyledonous plants have leaves spread out and exposed meristematic tissue, so that the toxin is directed to the growing point situated at the center of a rosette. While upright leaves of monocotyledonous plants enable plants to form a sheath around the meristem that protects it from receiving the herbicidal spray (Figure 1) [1]. Therefore, such morphological differences can be recruited to work with monocotyledon crops against dicotyledon weeds.

3.3. Chronological selectivity

Chronological selectivity utilizes the time period necessary for growing both weeds and crop plants. In other words, it depends upon the fact that some weeds are shallower rooted and grow more rapidly than the crop plants. In consequence, many of the potentially more competitive weeds that emerge before the crop can be sprayed by a foliage spray. The time of application of the herbicide is important for chronological selectivity to be successful. That means if the non-selective herbicides are applied too early, many of the germinating weed seedlings will escape and break through the soil surface; however, the crop may be damaged if those herbicides are applied too late (Figure 1) [1].

3.4. Positional selectivity

Positional selectivity is based upon the localization of weeds on the soil surface related to the main plant crop position. If seeds, tubers, etc., of the crops are large compared with those of the weeds, they become sown or placed quite deeply in the soil compared with the more shallow competitive weed seeds. Consequently, positional selectivity can often be achieved by spraying the soil surface with soil acting herbicides. These herbicides are able to destroy weed seeds growing in the top few millimeters of the soil, whereas the large seeds of the crop are protected by the fact that they are sown deeper in the soil. Bacteria and other microorgan-

isms attack and inactivate most herbicides when used at economic concentrations so the potential hazard to the crop is reduced (Figure 1) [1].

3.5. Placement selectivity

Placement selectivity can be achieved for non-selective substances when it is possible to direct a foliar spray in such a way that it makes contact only with the leaves of weeds and not the crop [2].

3.6. Genetic engineering

If the mode of action of an herbicide is known and the target proves to be a protein, genetic engineering may well allow the crop gene coding for that protein to be isolated. It is then possible to alter that crop gene so that it is less affected by the herbicide [2].This will be discussed in detail at the end of the chapter.

4. Herbicide interference with physiological and biochemical processes and plant response

Mode of action of herbicides can lead to various physiological and biochemical effects on both growth and development of the emerging seedlings as well as the established plants. These physiological and biochemical effects are followed by various types of visual injury symptoms on susceptible plants. The incidental damage extent depends on the selectivity of the herbicide as well as the applied concentration. The herbicide application is always recommended at a certain dose termed as recommended dose (R), above which, a great damage to the crop plant may be obtained. Overdoses threaten not only the crop plant but also the environment and human health. Some herbicides in lower than recommended doses may act as growth regulators for crop plants [1,2].

Even recommended doses may have undesired effects upon the crop. The undesired effects might occur in the form of chlorosis, defoliation, necrosis, morphological aberrations, growth stimulation, cupping of leaves, marginal leaf burn, delayed emergence, germination failure, etc. These injury symptoms may appear on any part of the plant.

The various physiological and biochemical processes affected by herbicides are grouped under five broad categories including: respiration, mitochondrial activities, photosynthesis, protein synthesis, nucleic acid metabolism, and hydrolytic enzyme activities. Most herbicides can affect at least one or all of these processes. The following discusses their effect on various biochemical processes.

4.1. Respiration and mitochondrial activities

Cellular respiration that takes place in mitochondria involves the synthesis of ATP and the transport of electrons and protons from respiratory substances to oxygen. Herbicides affect

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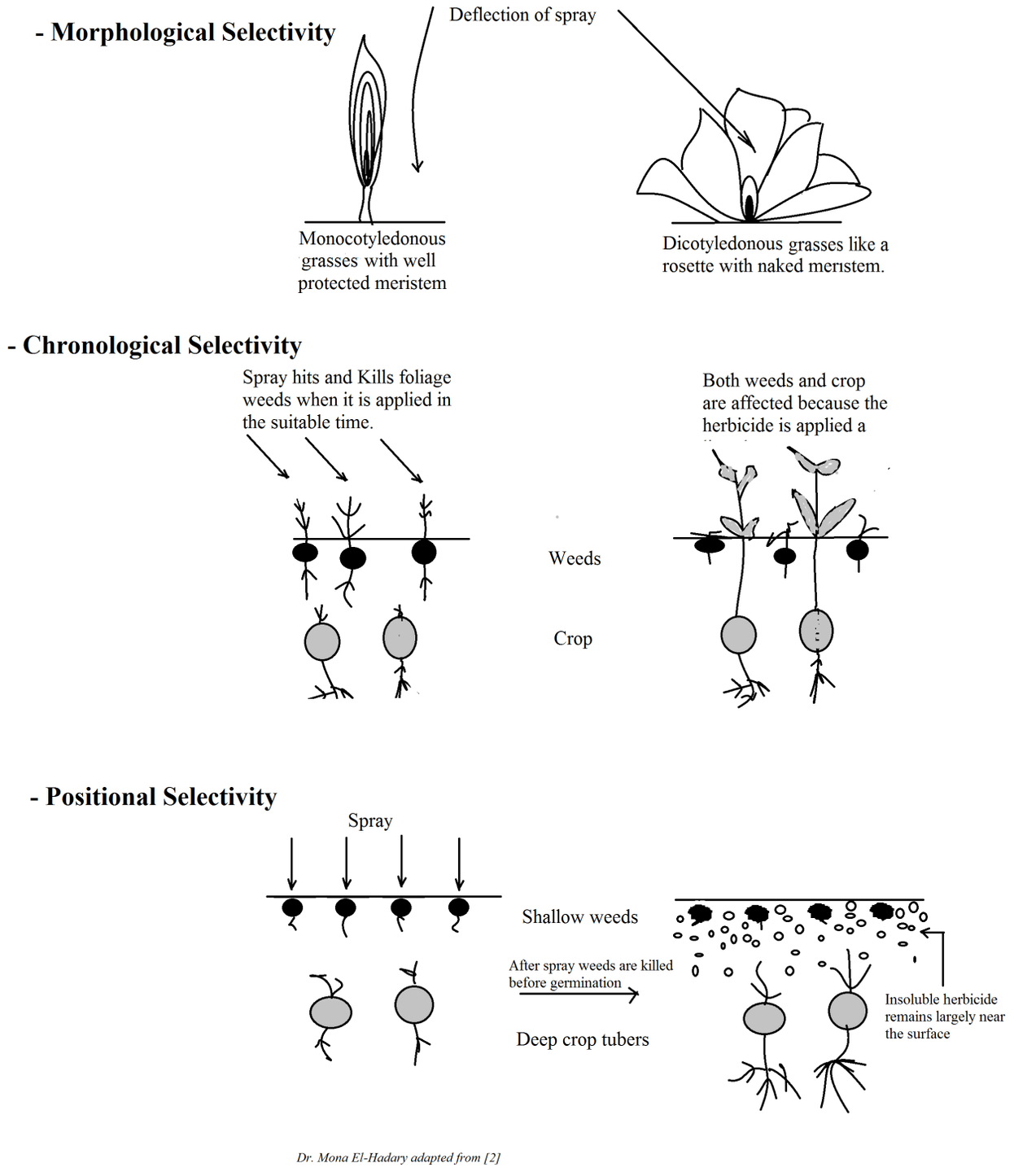

Figure 1. Factors Exploitable to Achieve Selectivity of Herbicides [1] as adapted from [2].

the mitochondrial activities by uncoupling the reaction responsible for ATP synthesis or interfering with electron transport and energy transfer. Uncouplers act on the membranes of the mitochondria in which phosphorylation takes place. Electrons leak through the membranes so that the charges that they normally separate are lost. As a result, energy is not accumulated for ATP synthesis [3].

4.2. Photosynthesis

Pigment content and photosynthetic activity are affected by herbicidal applications. The mode of action of herbicides on the photosynthesis process depends on the chemical group to which the herbicide belongs [3]. Herbicides affect chloroplast organization and pigment formation especially chlorophyll which is the principle absorbing pigment. Chlorophyll bleaching is a potent inhibitor for photosynthetic electron transport and CO_2 fixation.

Herbicides affect photosynthetic activity via different ways including photosynthetic pigments. The primary site of action is located at photosystem II (PSII) since they cause blocking of the Hill reaction. The oxygen evolution step is inhibited by interfering with the reducing side rather than the oxidizing side of PSII [4]. The inhibition of electron transfer through PSII causes a block in the whole transport chain as the inhibition of the noncyclic photophosphorylation and ATP synthesis. Consequently, the production of NADP is blocked and the function of the protective carotenoid system is prevented [5]. Urea herbicides inhibit both noncyclic and cyclic electron transport by forming a complex with oxidized form of an unknown component located in the electron transfer pathway close to PSII. This component also takes part in cyclic electron transport.

The photosystem I (PSI) also could be reduced by some herbicides but it requires much higher concentrations of the herbicide than that required for the inhibition of PSII. Since PSII precedes PSI and the former is blocked completely at concentrations which do not affect PSI.

In a study conducted by **El-Hadary** [1], it was observed that photosynthetic activity measured in wheat chloroplasts (variety Giza 163) was greatly reduced throughout the growth by using Brominal as an example for bromphenol herbicides but lower concentrations (1/4R, 1/2R and R) increased the activity. Pigment content represented as chlorophyll, a/b ratio and carotenoids showed a similar results [1]. In the same study, sulfonyl-urea herbicides such as Granstar were examined. It was observed that low Granstar concentrations stimulated the photolytic activity of chloroplasts while high concentrations reduced it. However, Granstar reduced a/b ratios throughout the growth stages, except a slight increase at the fruiting stage with 1/2R. Carotenoids were decreased only with high Granstar concentrations [1].

4.3. Protein and nucleic acid metabolism

Protein synthesis takes place mainly in three stages involving initiation, elongation and termination of the polypeptide chain. Blocking any one of these stages by the herbicide will cause inhibition of protein and nucleic acid synthesis. The herbicides that inhibit photosynthesis and ATP formation can lead to inhibition of protein synthesis as a secondary effect. The damage that is caused by an herbicide is governed by its chemical group. There are numerous studies that investigate effects of the herbicidal chemical groups upon protein and nucleic acid metabolism [2].

For instance, sulfonyl-urea herbicides block the biosynthesis of the branched chain amino acids in higher plants [6,7]. Aliphatic herbicides like Dalapon cause degradation of protein to ammonium compounds as detected in *Setaria lutescens* and sugar beets [8]. While acetamide herbicides such as propachlor, alachlor and prynaclor inhibited the protein content and RNA

synthesis as reported in barley [9-12]. Also, metalachlor inhibited protein synthesis in barley [13]. RNA and protein synthesis in tomato were found to be inhibited by propanil [14].

Benzoic and phenylacetic herbicides had variable effects on protein. For example, chloramben had no effect on RNA and protein synthesis on susceptible species [15]. On the other hand, it was suggested that foliar-applications of dicamba increased RNA and protein levels in susceptible plants by removal of histone from the DNA template [16]

Carbamate herbicide groups include a large number of herbicides such as asulam, barban, chlorpropham, propham, desmedipham and phenmedipham. [17]. Barban was found to inhibit protein synthesis and the degree of inhibition was related to the susceptibility of the plant species. For example, barban increased nucleotide content of wild oat shoots associated with disruption of RNA and protein synthesis. Chlorproham and propham inhibited amino acid incorporation into protein and induced a reduction in protein synthesis [18]. DNA, RNA and protein synthesis are also inhibited at high concentrations (10-3 M) of propham [19].

Fluridone, paraquat, perfluidone and propanil treatments were found to reduce soluble protein levels in soybean [20]. Paraquat and diquat readily act on proteins, modifying their structure and function (e.g.lysozome) since they interact with dibasic and dicarboxylic amino acids like ornithine and glutamic acid [21].

Oxadiazon at high doses inhibited protein synthesis in soybean while RNA and DNA synthesis were less sensitive to oxadiazon [22]. Combination of 2,4-D and glufosinate had an additive effect on protein synthesis in both sorghum and soybean [22]. On the other hand, sethoxydim, R- 25788 [N, N dichloroacetamide] or R- 28725 at low doses did not inhibit protein or RNA synthesis in cells of both sorghum and soybean but sethoxydim significantly inhibited DNA synthesis while R-25788 stimulated it [23]. Thus, the combined effects of sethoxydim and the two Safeners (R- 25788 and R- 28725) on protein and RNA synthesis were additive while on DNA synthesis they were antagonistic.

The application of haloxyfop to *Zea mays* and soybean cell suspension, increased ^{14}-C labeled free amino acids level and incorporation of ^{14}C leucine as a precursor revealed that haloxyfop did not inhibit protein synthesis [24].

Napropamide reduced DNA synthesis, RNA root cells of *Pea* and protein [25]. The inhibitory effect of napropamide on the mitotic cycle resulted from an inhibition in the synthesis of cell cycle specific protein. In contrast, 0.5 R, 1R and 1.5 R of metribuzin stimulated total and protein-N accumulation in soybean. Consequently, protein content was increased while RNA and DNA levels decreased [26]. Protein content of soybean yield was reported to be increased by application of 100 ppm GA_3 (gibbrellic acid) and 2g/L Librel separately or together [27].

Metoxuron had a remarkable inhibition on the total protein biosynthesis, while bromoxynil accelerated the biosynthesis of low molecular proteins (water-soluble proteins) and inhibited the biosynthesis of high molecular proteins (sodium hydroxid soluble proteins) in wheat (*Triticum aestivum*, var. Sakha 69) [28]. Bromoxynil at low doses (0.4 and 0.8 kg / fed) enhanced protein content and RNA synthesis in wheat plants after 30 to 60 days from foliar spraying [29].

Nitrogen in wheat grains, consequently protein, was found to be increased by treating wheat plants with Brominal at the 2-leaf stage [30]. Different bromoxynil levels increased the protein percentages in wheat grains [31]. The foliar spray with bromoxynil increased significantly the protein content in wheat grains [32]. Application of bromoxynil at the full recommended rate significantly increased grain nitrogen and proteins in both wheat and barley. The increase was evaluated by multiplying grain nitrogen by 5.7 as a factor in both wheat and barley [33]. Protein content in wheat vegetation (Giza 163) was significantly increased at the vegetative stage and flowering stage while decreased at the fruiting stage as a response to either low or high Brominal treatments [1]. In contrast, the protein content of wheat root was reduced. Also, protein profiling of grains is greatly altered with an induction for 19kDa and 25kDa but an inhibition for 66kDa, 100kDa and 110kDa was obtained [1].

The action of urea herbicides on protein and nucleic acid metabolism has been reported by many researchers. Although fluometron can cause an increase in the low molecular weight fraction of DNA, RNA and protein synthesis [34], diuron and monuron inhibited the same parameters as reported [35]. However, the monomethylated derivative of isouron [N-[5-(1,1-dimethy ethyl-3-iso) (azol]-N-methylurea] suppressed the protein synthesis in soybean[36].

Sulfonylurea herbicides were found to inhibit branched chain amino acids valine, leucine and isoleucine (e.g. Granstar; DPX- L 5300; tribenuron) [6, 7]. Aflon (urea herbicide), when sprayed at 1/2 R and R doses on *Phaseolus vulgaris,* induced a DNA increase in both shoot and root while RNA content was increased in shoot only [37]. Moreover, RNA content of roots was mostly decreased in response to R and 2R aflon treatments but increased as a result of the 1/2 R application [37]. Protein content of the wheat shoot system was increased with all Granstar concentrations at the vegetative stage and with low concentrations (1/2R and R) at both flowering and fruiting stages. In contrast, protein levels were decreased with 5/2R at the flowering stage and with 3/2R and $2R^-$ and 5/2R at the fruiting stage [1]. Granstar treatments reduced the contents of root proteins at the vegetative stage and flowering stages but increased it at the fruiting stage. Protein profiling of grain proteins exerted an induction for 19kDa and 25kDa and complete suppression for 66kDa, 100kDa and 110KDa [1].

4.4. Hydrolytic enzyme activities

Enzymes of plants were affected greatly by herbicide treatments and their effect differs according to the chemical group to which the herbicide belongs. The following examples represent some effects of herbicides on the enzyme activities of some plant species.

One of the major metabolic processes that take place during seed germination is the production of hydrolytic enzymes such as α-, β-amylases that degrade stored carbohydrates into simple sugars. The production of hydrolytic enzymes requires the synthesis and presence of proteins, polyribosomes and nucleic acids. Thus, an effect of the herbicide on protein formation as mentioned above, would affect the synthesis of the hydrolytic enzymes [1, 3]. **El-Hadary** [1] reported that use of either Brominal or Granstar at different levels below and above the recommended rate induced stimulation for amylolytic enzyme activity (α and β-amylase); however, an incidence of a slight reduction in β-amylase activity was observed with 2R and higher doses of Granstar [1].

Dalapon, which is an aliphatic herbicide, did not affect the activity of hydrolytic enzymes like protease, α- amylase and dipeptidase in barley seeds [38]. Acetamides such as alachlor, propachlor and prynachlor which all were applied at pre-emergence caused an inhibition for seed germination in barley by reducing the synthesis of α-amylase enzyme [39].

It was reported that propaclor inhibited the gibberellic acid (GA_3) induced production of α-amylase in barley seeds [40]. Similarly, alachlor, propachlor and prynachlor were found to inhibit α-amylase as well as protease synthesis in barley seeds [41, 42]. It was suggested that these herbicides may act as repressors for gene action preventing the normal expression of the hormonal effect of GA_3 through the synthesis of DNA-dependent RNA. This was confirmed when higher levels of GA_3 overcame alachlor inhibition by removing the repressor effect [42]. In addition, the effect of these acetamide herbicides on α- amylase and protease was suggested to be secondary and these herbicides possibly act on the biosynthetic reactions (like protein synthesis) required for the synthesis of these hydrolytic enzymes.

Chloroamben and dicamba, which belong to the benzoic and phenylacetic acid herbicide groups, were found to inhibit GA_3-induced α-amylase synthesis and the development of amylase activity in barley seeds [40, 43]. This agrees with effect of trifluarlin, as an example for dinitroanilines, which was found to inhibit the *de novo* synthesis of hydrolytic enzymes such as protease [44] and dipeptidase in squash cotyledons [45], phytase in barley seedlings, squash cotyledons and maize embryos [39], and α-amylase in barley seeds [40].

Nitriles such as bromoxynil and ioxynil also inhibited proteolytic and amylolytic enzyme activities [46, 45]. Also, thiocarbamate herbicides were found to inhibit GA_3- induced α-amylase synthesis in susceptible weeds [17]. Acifluorfon was found to stimulate the activity of chalcone synthase, phenylalanine ammonia lyase and isoflavone 7-0- glucosy transferase which are responsible for the accumulation of isoflavonoids in soybean leaves [47].

The increase of galactonolactone oxidase was reported in common beans as a result of acifluorfen application; this enzyme is responsible for lipid peroxidation. Acifluorfen was found to increase the activity of galactonactone reductase, which prevented further oxidation of lipids [48]. Other herbicides, alachlor and glyphosate, were observed to inhibit 5- enolpyruvyl shikimate-3-phosphate (EPSP) synthase enzyme. This enzyme is responsible for the synthesis of all cinnamate derivatives (intermediates in flavonoids biosynthesis pathway) leading to reduced flavonoid synthesis in higher plants [49].

Sulfonylureas herbicides act by inhibiting acetolactate synthase enzymes, thereby blocking the biosynthesis of the branched chain amino acids in higher plants [7]. According to **Gronwald** [50], carbomothioate herbicides inhibited one or more acyl- CoA elongase enzymes which catalyze the condensation of malonyl CoA with fatty acid acyl-CoA substrates to form a very long chain fatty acid, used in the synthesis of surface lipids.

The effects of triazine, urea and nitroaniline herbicides on amylase and acid proteolytic activities of wheat grain cultivars, Salwa, Grana and Liwilla were studied by **Wybieralshi and Wybieralska** [51]. The studied herbicides were found to inhibit amylase activity in Salwa and Liwilla, but increased it in Grana. Acid proteolytic activity in Liwilla and Salwa was reduced especially by Igran 80 (terbutryn) and Dicuran 60 (Chlorotoluron), while the activity in Grana

was not affected. In contrast, amylase, dehydrogenase, cellulase and xylanase activities were increased by application of the herbicides Pyramin (chloridazon), Ro-neet (cycloate) and Venzar (lenacil) when applied on the soil with 5% (w/w) addition of wheat straw [52]. Other studies suggested that application of SAN 9789 (norflurazon) as a metabolic inhibitor to *Sinapis alba* seedlings destroyed the chloroplasts but had no effect on α-amylase activity. This is due to the fact that α-amylase is a cytosolic enzyme [53].

The levels of leaf β-amylase and starch debranching enzyme in pea seedlings were found to slightly decrease in response to norflurazon-treatment [54]. However, inhibitors of chloroplastic functions, i.e.; diuron (DCMU), atrazine, tentoxin, paclobutrazol and San 9785 (4 -chloro-5-(dimethylamino)-2-phenyl-3 (2H)- pyridazinone) caused either no or only slight increases in α-amylase activity. In contrast were the inhibitors of plastidic protein synthesis lincomycin and chloramphenicol that cause an increase in α-amylase activity in pea seedlings. It is concluded that there was an inverse relationship between α-amylase activity and chlorophyll concentration in pea petals and stems [55]. Similarly an inhibition of α-amylase induction in barley seeds was reported [56]. Also, Li found that juglone decreased the content of total soluble protein and α-amylase activity induced by gibberellin by 74% and 78% in the aleuron cells of barley. It was concluded that juglone may be a metabolic inhibitor which prevents many (if not all) physiological and biochemical processes involving SH-groups in compounds such as amino acids, peptides and enzymes [57].

The activities of α-and β-amylases of castor bean and maize Giza 2 seedlings and adult plants supplemented with low concentration (0.5-2.5 μg/g) of metribuzin either alone or in combination with NaCl at 50 μg/g were increased significantly [58] but higher metribuzin concentration (5-10μg) had an opposite response. Application of 1.5-4.5kg/ha thiobencarb and butachlor six days after transplanting of 30-day-old rice seedlings affected the enzyme activities of the seedlings whether they were grown alone or with the competitive barnyard grass [59]. Moreover, both herbicides reduced α-amylase activity by increasing the concentration but a sharp increase in α-amylase activity was noted at 96h post-treatment in both species. In addition, protease (proteinase) activity was maximized after post-treatment at both 48h.and 24h in rice and grass, respectively.

Butachor (1000-3000 g/ha) and oxyfluorfen (100-300g/ha) effect on α-amylase activity and chlorophyll content in 46 rice cultivars was dependent on the degree of tolerance of each cultivar [60]. It was concluded that rice cultivars ADT-37, ASD-16 and ASD-18 were highly tolerant to butachor, whereas ADT-36, ADT-38 and PY-3 were highly susceptible. However, tolerance to oxyfluorfen was high in ASD-18 and AS-18696, while IR-50 was highly susceptible [60].

4.5. Lipid synthesis and oxidation

Substituted ureas, uracils, triazine, benzonitriles and bipyridyls markedly accelerated the photo-oxidations (lipids- per-oxidation) but peroxidation was completely prevented by NADH or NADPH [5]. Lipid peroxidation in higher plants (Duranta and Cassia) was induced by oxyfluorfen [61] but the peroxidative cell damage is controlled by antioxidative systems such as vitamins “C” and “E”.

Lipid peroxidation and galactonlactone oxidase increased in response to the treatment of *Phaseolus vulgaris* leaves with acifluorfen [48] and the activity of glutathione reductase also increased to prevent further oxidation. Gronowald studies on herbicides concluded that the carbothioates group impaired the synthesis of surface lipids (waxes, cutin, and subrin) by inhibiting acyl- CoA elongases while chloroacetamide herbicides inhibited *de novo* fatty acid biosynthesis. Similarly, pyridazinones herbicides decreased the degree of unsaturation of plastidic galactolipids while aryloxyphenoxy pypropionic acid and cyclohexanedione herbicides inhibited *de novo* fatty acid synthesis. The target site for all these classes is the enzyme acetyl-CoA carboxylase [50].

The total lipid content as well as *gluco*-and *phospho*-lipid content of maize seedlings markedly decreased by application of perfluidone while in sunflower cotyledons total lipids were not affected but glycolipids increased at the expense of phospholipids [62]. Also, a decrease in lipid synthesis in soybean by Isouron was reported [36] but an increase in seed oil of soybean was obtained by 0.5R or 1R metribuzin application [26].

4.6. Carbohydrate content

Carbohydrate content is one of the most affected parameters in response to herbicide application**. Yakout** [28] demonstrated that treating wheat (*Triticum aestivum* var. Sakha 69) with metoxuron showed a slight reduction in the available carbohydrates with relatively no change in sucrose content while bromoxynil showed an increase in different carbohydrate levels. Also, the total reducing substances (may include sugars, phenolic substances, ascorbic acid, organic acid, etc.) were increased for both treatments [28].

Inhibition of the accumulated reducing sugars, sucrose and polysaccharides, in soybean leaves was observed in response to 1R and 1.5R metribuzin application and, consequently, seed carbohydrate content decreased with increasing metribuzin concentration [26]. Terbytryn herbicide was found to decrease starch content and increase sugar content in pre-emergence and post emergence applications [63]. On the other hand, bromoxynil was reported to significantly increase soluble and total carbohydrates at low doses while a higher dose (1.2 kg/Fed) inhibited their synthetic rate in wheat plants [29]. Similarly, the results of **El-Hadary** [1] found that *mono-, di- and poly*-saccharides and, consequently, total carbohydrates were increased with low doses but decreased with high doses of either Brominal or Granstar [1]. The incidental increase with low concentrations was attributed to that some herbicides act as growth regulators in low doses.

Urea herbicides including afalon-S at low doses of 1/2R and R increased the soluble and insoluble sugar contents of shoots at different stages of growth and development of *Phaseolus vulgaris* while a reverse situation was obtained in the case of a 2R application. The root tissue treated with various concentrations suffered from an obvious decrease in the content of the different carbohydrate fraction relative to those of the control [37].

The content of reducing sugars and sucrose of *Ricinus communis* cultivar Balada and maize cultivar Giza 2 seedlings and adult plants supplemented with low concentrations (0.5-2.5μg/g) of metribuzin either alone or in combination with NaCl at 50μg/g were increased significantly

but decreased in response to higher concentrations (5-10μg). On the other hand, polysaccharide content of *R. communis* and maize seedlings as well as adult plants were significantly decreased in response to low concentrations of metribuzin and increased significantly at higher concentrations either alone or in combination with NaCl. Total carbohydrate content detected in *R. communis* treated with metribuzin were greater than those detected in presence of herbicide and NaCl combination [58].

Thiobencarb and butaclor herbicides when applied at 1.5-4.5 kg/ha after transplanting 30 days old rice seedlings and barnyard grass grown alone or with rice were found to have no effect either on total carbohydrate or starch and reducing sugars in rice and grass [59].

4.7. Plant growth response and yield

Plant growth and yield are greatly affected by herbicidal applications depending on the age, tolerance, dose and the active chemical group of the herbicide. The author in a previous work pointed that Brominal application on wheat induced an increase in the number of grains per spike with 1/4 R. 1/2R and R while higher doses caused a significant reduction [1]. Also, grain yield showed a detectable reduction in monosaccharides, disaccharides, polysaccharides and, consequently, total carbohydrate levels with all Brominal concentrations [1].

The percentage of germination and seedling growth of barley was decreased greatly by applications of bromoxynil [64]. But the same herbicide in different concentrations encouraged wheat growth [31]. Also, growth parameters such as plant height, weight and leaf area of wheat plants at 75 days after sowing were increased significantly by foliar application of bromoxynil at rate of 1.0 L/Fed [32, 65]. Moreover, a good seedling establishment of wheat was obtained by combinations of bromoxynil and fenoxaprop [66]. Low metribuzin concentrations (0.5-2.5μg/g) either alone or in combination with NaCl (50 μg/g) caused an increase in different growth parameters such as leaf area, length of shoot and root, water content and dry matter accumulation in both *Ricinus communis* cultivars, and maize cultivars Giza 2 throughout the different growth stages [58]. In contrast, the higher metribuzin concentration (5-10μg) affected the same parameters oppositely [58].

Productivity of the plant is affected in terms of 100 grains weight in response to herbicides treatment. The yield of wheat grains (var.Sakha 69) increased by bromoxynil application [28]. A dose of 1.5 kg/ha of bromoxynil brought an increase in weight of 100 grains [30,67]. The highest yield was obtained when one liter/fed bromoxynil was applied at the third-leaf stage [68]. The number of wheat grains/ear and grain yield were increased at a low dose (0.8kg/ fed.) of bromoxynil [29,69] while a higher dose of the same herbicide (1.2 kg/ fed) reduced the yield of wheat varieties; i.e. Sakha 69, Giza 157 and Giza 160 [29]. On the other hand, it was noticed that higher doses of bromoxynil resulted in a marked increase in both yield and grains/ear when crops were poorly developed at the time of spraying [70]. However, the application of 2.5, 3.0 liter bromoxynil /ha at the third-leaf and flowering stages on wheat significantly decreased the grain yield [71] as well as the number of spikes per plant, main spike length, weight of 100 grains and straw per plant [32].

Herbicidal effects may be varied when they are applied in combination. For example, a marked increase was observed in the grain yield, ears/plant and number of ears in barley by using a combination of bromoxynil, ioxnil and mercoprop [72]. An increase of about 20% was recorded in grain wheat yield when oxitril 4, which is a combination of oxitril and bromoxynil, was used at 130g/liter and applied at rates of 1.5,4 and 5 liters/ha [73]. In winter wheat a marked increase in yield was mentioned in response to half rate applications of various commercial herbicides (active ingredients bromoxynil, ioxynil, mocoprop, cyanazine, fluroxypyr, metasulfuron-methyl, and clopyralid) [74].

Urea herbicide such as Granstar (metasulfuron- methyl 75% water dispersible granules) was found to suppress the growth rate of wheat and barley by about 20% while weeds were completely destroyed[75]. Its application with a dose of 20-40 g/ha in 200-500 liter/ha prior to planting resulted in 50% suppression [76]. The author in a previous work applied Granstar at a dose of 0.5R, 1R, 1.5R and 2R on wheat at 40-days old and reported an increase in grains no./spike [1]. However, a great decrease in monosaccharides, disaccharides, polysaccharides and, consequently, total carbohydrate levels was obtained in wheat grains with both low and high Granstar concentrations [1]. Also, chlorsulfuron was mentioned to reduce both the third leaf growth rate and shoot dry weight of wheat seedlings but not the root dry weight [76].

The urea herbicide metoxuron was reported to decrease wheat grain yield (var. Sakha 69) [28]. It was found that 100-seed weight of soybean was decreased by using metribuzin at rates of 0.5R, 1R and 1.5R [26]. Wheat yield was markedly increased by using tribenuron at a rate of 0-125g [77]. However, sulfonylurea herbicides, Chisel [Chlorosulfuron+thifensulfuron - methyl] and Granstar, significantly increased the productive tillering in some wheat varieties [78]. Application of trifluralin alone in the spring followed by some post herbicides resulted in a reduction in vegetative growth, shoot dry weight and wheat grain yield [79]. An application of 0.126 mM perfluidon herbicide was reported not only to decrease both fresh and dry weight but also shoot length of maize seedlings [62].

5. Hazardous action of herbicides in the agricultural environment and human health

Although the benefits gained from herbicides usage in weeds control, herbisides have undesired effects on man health and environment. Their residues remain in the soil for many years, affecting crops, water canals, grazing animals and human health and even the pollution of air.

Herbicides and pesticides have been suspected by the "National Cancer Research Institute" as a probable cause of certain cancers especially cancers of the brain, prostate, stomach and lip, as well as leukemia, skin melanomas and Hodgkin's lymphoma [80]. They also cause reproductive problems as well as infertility and nervous system diseases. The National Academy of Sciences reported that infants and children, because of their developing physiology, are more susceptible to the negative effects of herbicides and pesticides in comparison to adults. Herbicides may cause human poisoning since they affect humans through three mechanisms

of entry: ingestion, inhalation and dermal absorption. In under-developed countries, the least expensive pesticides are utilized due the inability of farmers to purchase more expensive, safer products. As a byproduct of pesticide use, farmers and their families are affected daily with health problems directly resulting from pesticide exposure [81]. Herbicide toxicity and risks are not only limited by their direct use but can also present risks indirectly. Indirect risks are represented by herbicidal traces that remain in the edible plants themselves as well as the residues in the soil that may remain for a number of years before it can be degraded. Moreover, the leakage of these herbicides and their residues in water canals, vaporization and sublimation in air may be poisonous to the surrounding living organisms.

6. Natural herbicides

Allelopathy phenomenon serves the agricultural community so much. The following section discusses the related concepts to allelopathy and recruiting it as natural herbicides for weed management to be an alternative or to minimize conventional herbicide use.

6.1. Allelopathy term

Allelopathy is a natural biological phenomenon of interference among organisms in such a way that an organism produces one or more biochemicals that influence the growth, survival, and reproduction of other organisms. Allelopathy is the favorable or adverse effect of one plant on another due to direct or indirect release of chemicals from live or dead plants (including microorganisms).

6.2. Allelochemical term

Allelochemicals, or allelochemics, are a subset of low molecular weight secondary metabolites such as alkaloids, phenolics, flavonoids, terpenoids, and glucosinolates which are produced during growth and development but are not used by the allelopathic plant [82]. Allelochemicals may have beneficial (positive allelopathy) or detrimental (negative allelopathy) effects on the target organisms. Allelochemicals with negative allelopathic effects contribute in plant defense against herbivory. Also, allelochemicals could be recruited in weed management as alternatives to herbicides.

Allelochemicals are listed as six classes [83] that possess actual or potential phytotoxicity. The classes are namely alkaloids, benzoxazinones, cinnamic acid derivatives, cyanogenic compounds, ethylene and other seed germination stimulants, and flavonoids which have been isolated from over 30 families of terrestrial and aquatic plants. Like synthetic herbicides, there is no common mode of action or physiological target site for all allelochemicals.

6.3. Allelochemical occurrence

Allelochemics are present in different parts of the plant; leaves, flowers, fruits, stems, bark, roots, rhizomes, seeds and pollen. They may be released from plants into the environment

through volatilization, leaching, root exudation, and decomposition of plant residues. Rainfall causes the leaching of allelopathic substances from leaves which fall to the ground during period of stress, leading to inhibition of growth and germination of crop plants [84, 85].

6.4. Allelochemical classification and biosynthesis

According to the different structures and properties of allelochemicals, they can be classified into the following categories: water-soluble organic acids, straight-chain alcohols, aliphatic aldehydes, and ketones; simple unsaturated lactones; long-chain fatty acids and polyacetylenes; quinines (benzoquinone, anthraquinone and complex quinines); phenolics; cinnamic acid and its derivatives; coumarins; flavonoids; tannins; steroids and terpenoids (sesquiterpene lactones, diterpenes, and triterpenoids) [86]. The biosynthetic pathways of the major allelopathic substances are shown in Figure 2 [87].

6.5. Allelochemical interference and biological activity

The allelochemical interference implies their interference with each other as well the interference with other surrounding plants. Several chemicals can be released together and may exert toxicities in an additive or synergistic manner. Allelopathic interferences often result from the mixing action of several different compounds. Allelopathic plant extracts can effectively control weeds since mixtures of allelopathic water extracts are more effective than the application of single-plant extract. Combined application of allelopathic extracts and reduced herbicide dose (up to half the standard dose) give as much weed control as the standard herbicide dose in several field crops. Lower doses of herbicides may help to reduce the development of herbicide resistance in weed ecotypes [88]. Allelopathy thus offers an attractive environmentally friendly alternative to pesticides in agricultural pest management [88].

Response of the receiver plants to allelochemicals is not only concentration dependent but also controlled by the biochemical pathway in the receiver plant. Generally, low concentrations of allelochemicals are stimulatory while it is inhibitory with higher concentrations [89]. Allelochemical concentrations in the producer plant may also vary over time and in the plant tissue produced. Foliar and leaf litter leachates of Eucalyptus species, for example, are more toxic than bark leachates to some food crops. Typically, allelochemical concentration in field situations is below the required inhibitory level that can affect sensitive plants.

Receiver plant response to antagonistic allelochemicals is detected as certain signs on growth and development of the plants that are exposed to allelochemicals. The effect includes the inhibition or retardation of germination rate; seeds darkness and swelling; root or radicle reduction, curling of the root axis, lack of root hairs; increased number of seminal roots, swelling or necrosis of root tips; shoot or coleoptile extension; discolouration, reduced dry weight accumulation; and lowered reproductive capacity. These morphological effects may be secondary for primary events due to interference with different biochemical pathways of the receiver plant [90].

Biological activity of allelochemicals could be increased by some modifications so the end product could be more active, selective, or persistent. This is attributed to the potential

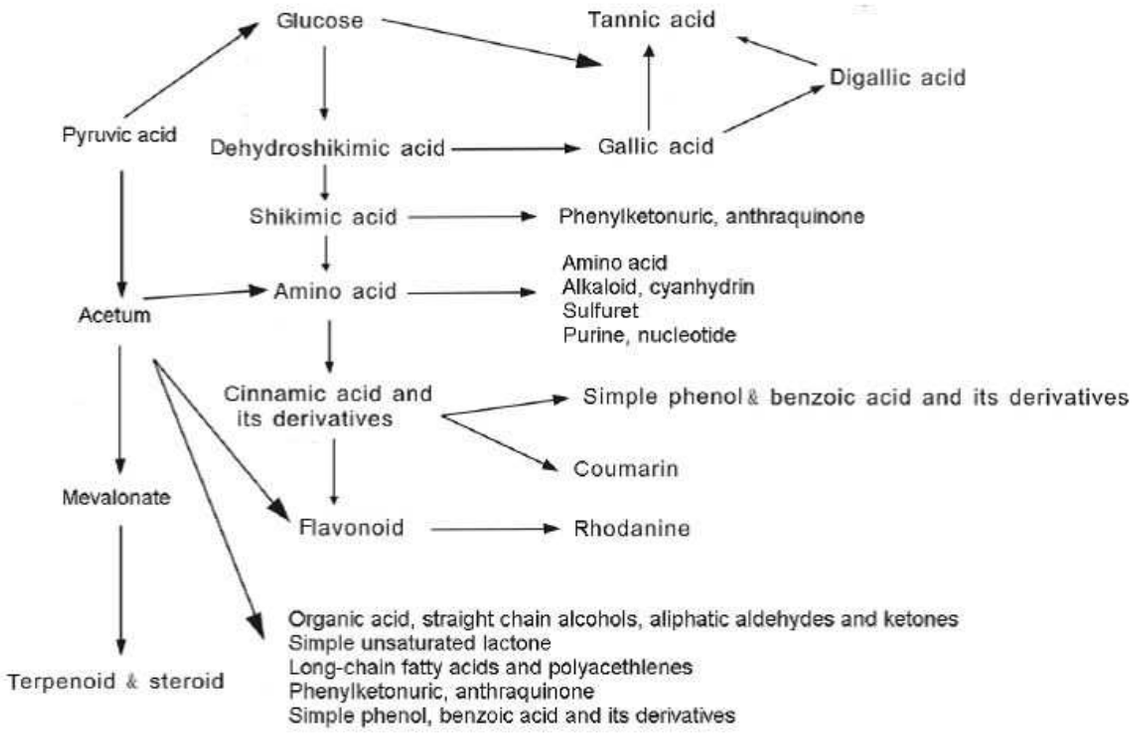

Figure 2. The Biosynthetic Pathways of the Major Allelopathic Substances [87]

phytotoxicity of alkaloids, benzoxazinones, cinnamic acid derivatives, cyanogenic compounds, ethylene and other seed germination stimulants, and flavonoids that always represent the secondary products of allelopathic plants. Biodegradable natural plant products rarely contain halogenated atoms and possess structural diversity and complexity, constituting one such class of chemicals and these can act directly as herbicides or may provide lead structures for herbicidal discovery [91]. Selection of allelopathic plants is a good and commonly used approach for identification of plants with biologically active natural products [91].

Different crops such as beet (*Beta vulgaris* L.), lupin (*Lupinus lutens* L.), maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.) and barley (*Hordeum vulgare* L.) are known to have an allelopathic effect on other crops (Rice, 1984b). For instance, some wheat cultivars were found to significantly inhibit both germination and radicle growth of annual ryegrass. The allelopathic potential of wheat cultivars was positively correlated with their allelochemical (total phenolics) content [92]. However, different allelopathic compounds of some crops important in weed management are presented in Table 1 [93].

6.6. Allelopathic plants impact

There are some examples of plants that act as natural herbicides, such as black walnut, sunflowers, sagebrush and spotted knapweed. An herbicidal chemical called catechin was extracted from the roots of spotted knapweed and can be synthesized on a larger scale and applied to a number of other invasive plants due to selectivity. Another popular species with

Crops	Scientific name	Allelochemicals
Rice	Oryza sativa L.	Phenolic acids
Wheat	Triticum aestivumL.	Hydroxamic acids
Cucumber	Cucumis sativus L.	Benzoic and Cinnamic acids
Black mustard	Brassica nigra L.	Allyl isothiocyanate
Buck wheat	Fagopyrium esculentum L.	Fatty acids
Clovers and	*Trifolium spp.*	Isoflavonoids and Phenolics
Sweet clover	*Melilotus spp.*	Phenolics
Oats	Avena sativa L	Phenolic acids and Scopoletin
Cereals	-	Hydroxamic acids
Sudangrass		Phenolic acids and Dhurrin
Sorghum	Sorghum bicolor L.	Sorgoleone

Table 1. Allelochemicals of Some Important Crops

natural herbicide abilities is the black walnut tree whose leaf extraction is often used in commercially-produced natural herbicides [94].

Other natural pre-emergent herbicides are used to control weed growth such the natural herbicide corn gluten meal. Corn gluten meal was originally developed as a medium for growing fungus, but its inhibitory effect upon the germination of weeds and grasses was detected. A cover crop of rye could work as a natural herbicide between soybean crops [94].

Herbicidal effects have been identified and quantified for more than twenty allelochemicals in *Vulpia* residues. Those present in large quantities possessed low biological activities, while those present in small quantities possessed strong inhibitory activities. Interference between different allelochemicals controls the overall phytotoxicity of *Vulpia* residues which varies according to the individual chemical structure and occurred quantity. This interference provides a pattern for suggested artificial combinations of these allelochemicals prepared in aqueous solution. Biological tests for different combinations of *Vulpia* extracts demonstrated the existence of strong synergistic effects among the identified allelochemics. Moreover, exploration of the composition of a cluster of allelochemicals, which are simple in structure, possess various biological activities and few barriers to synthesis and production; this provides an alternative option for developing new herbicides from individual plant allelochemicals [94].

Selective activity of tree allelochemicals on crops and other plants has also been reported. For example, *Leucaena leucocephala*, the miracle tree promoted for revegetation, soil and water conservation and animal improvements in India, also contains a toxic, non-protein amino acid in leaves and foliage that inhibits the growth of other trees but not its own seedlings. *Leucaena* species have also been shown to reduce the yield of wheat but increase the yield of rice. Leachates of the chaste tree or box elder can retard the growth of pangolagrass but stimulate growth of bluestem, another pasture grass. Examples that are shown in Table 2 represent some allelopathic plants and their impact as reported in published research [95].

6.7. Allelochemical modes of action

Allelochemical action goes mainly through affecting photosynthesis, respiration cell division, enzymes function and activity, endogenous hormones and protein synthesis. This suggests allelochemical action on the molecular level and gene expression [86]. Some phenolics such as ferulic acid and cinnamic acid can inhibit protein synthesis or amino acid transport and the subsequent growth of treated plants. This is attributed to the ability of all phenolics to reduce integrity of DNA and RNA [86]. A series of physiological and biochemical changes in plants induced by phenolic compounds are shown in Figure 3 [87].

Allelopathic Plant	Impact
- Rows of black walnut interplanted with corn in an alley cropping system	- Reduced corn yield attributed to production of juglone, an allelopathic compound from black walnut, found 4.25 meters from trees
- Rows of Leucaena interplanted with crops in an alley cropping system	- Reduced the yield of wheat and tumeric but increased the yield of maize and rice
- Lantana, a perennial woody weed pest in Florida citrus	- Lantana roots and shoots incorporated into soil reduced germination and growth of milkweed vine, another weed
- Sour orange, a widely used citrus rootstock in the past, now avoided because of susceptibility to citrus tristeza virus	- Leaf extracts and volatile compounds inhibited seed germination and root growth of pigweed, bermudagrass, and lambsquarters
- Red maple, swamp chestnut oak, sweet bay, and red cedar	- Preliminary reports indicate that wood extracts inhibit lettuce seed as much as or more than black walnut extracts
- Eucalyptus and neem trees	- A spatial allelopathic relationship if wheat was grown within 5 m
- Chaste tree or box elder	- Leachates retarded the growth of pangolagrass, a pasture grass but stimulated the growth of bluestem, another grass species
- Mango	- Dried mango leaf powder completely inhibited sprouting of purple nutsedge tubers.
- Tree of Heaven	- Ailanthone, isolated from the Tree of Heaven, has been reported to possess non-selecitve post-emergence herbicial activity similar to glyphosate and paraquat
- Rye and wheat	- Allelopathic suppression of weeds when used as cover crops or when crop residues are retained as mulch.
- Broccoli	- Broccoli residue interferes with growth of other cruciferous crops that follow

Table 2. Examples of Allelopathy from Published Research.

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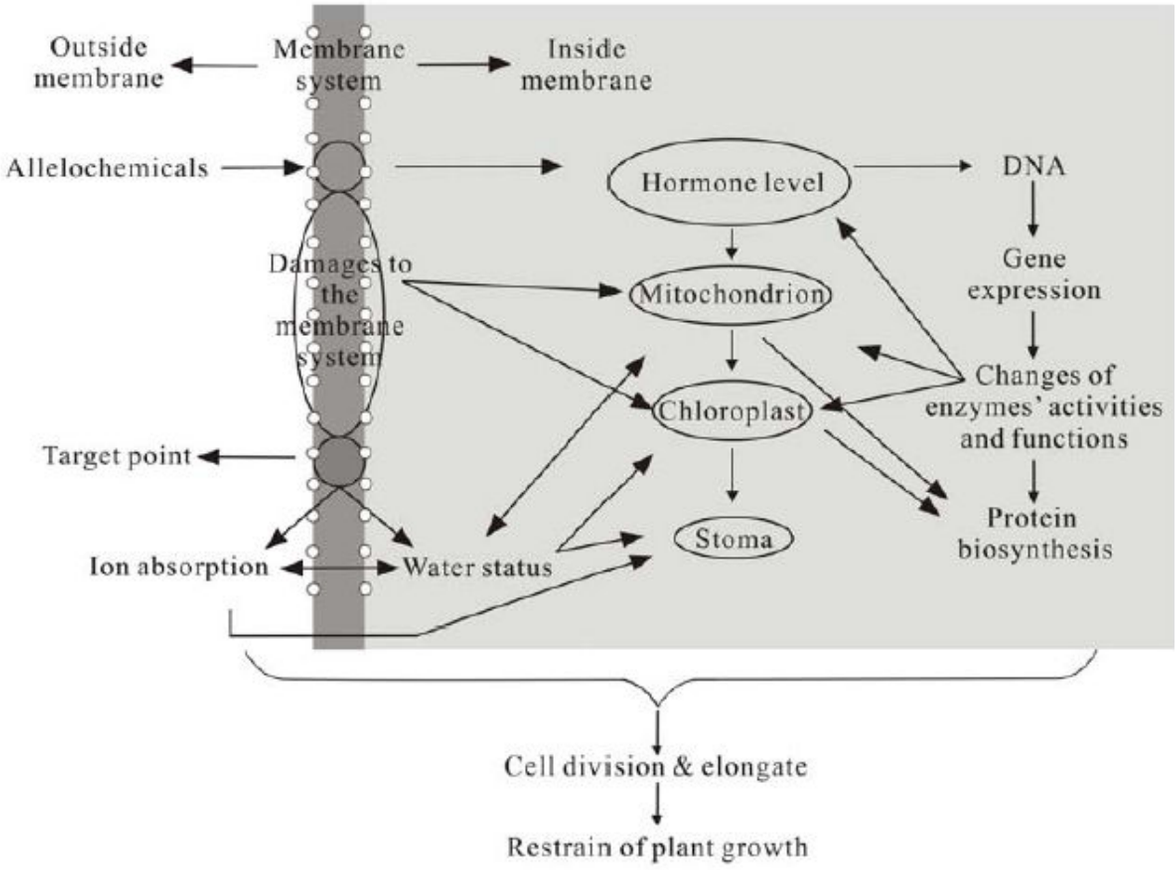

Figure 3. Mechanism of Allelochemicals [87].

6.8. Strategies of allelopathic plants application as natural herbicides

The strategy of allelochemical application is based on their antagonistic or synergistic action. Antagonistic properties of allelopathic plants are utilized in companion cropping system. Growing a companion plant which is selectively allelopathic against certain weeds and does not interfere appreciably with crop growth can greatly reduce weed establishment [96].

The interaction of weeds with crops may be positive; for instance, controlled densities of wild mustard (*Brassica campestris* L.) were interplanted with broccoli (*Brassica oleracea* var. Premium crop), crop yield increased by as much as 50% compared with broccoli planted alone [97].

Allelochemicals may be utilized as stimulators to weed seed germination before sowing the main crops, so that the germinated weeds could be eradicated easily. *Striga asiatica* is a good example for this case since it grows as a parasite to cereal grains in the southeastern United States. *Striga* normally germinates in response to compounds released from its host plants [98]. A germination stimulant, a p-benzoquinone compound from a natural host (sorghum) for *Striga* was identified. This stimulatory compound is used to induce germination of *Striga* and eradicate it before cropping its host. Ethylene was found to be a very effective germination stimulant. Also, ethylene stimulates *Striga* to germinate in the absence of a host [99] since its

use as a gas at about 1.5kg/ha has been used effectively via a soil injection to trigger "suicidal" germination of *Striga* and to deplete the numbers of dormant seeds in soil [100].

6.9. Limitation of using allelopathic plants as herbicides

Recruiting allelopathy in weed management is limited by both the allelopathic plant itself and the environment. Production, release and phytotoxicity of allelochemicals are altered by biotic and abiotic soil factors [101, 102] such as plant age, temperature, light and soil conditions, microflora, nutritional status, and herbicide treatments. Toxicity of allelochemicals may be either cleared or increased after releasing into the soil by action of microbes [103] since the toxicity is influenced by soil texture. For instance, amounts of water-soluble phenolics in *P. lanceolata* leaf leachate amended soil varied depending on the soil textural classes if it is clay, sandy-loam, sand, or silty-loam [104]. Some allelopathic agents are active only under hot and dry climates as they work in the vapor phase such as monoterpenes because the high vapor density of the essential oils may penetrate into soil, affecting adversely the under growing plants [105].

High costs for synthesizing many allelochemicals stands as a limiting factor for utilizing allelochemicals. Also, the hazardous action of allelochemicals on human beings limits their use. They may be toxic [91] carcinogenic [106] or even cause thyroid, liver and kidney diseases in monogastric animals [107].

Allelopathic potentiality of some plants is influenced either by the availability or deficiency of nutrient. The deficiency of nutrients favors the production of secondary metabolites. For example in aerobic P-deficient soil, rice roots excrete organic anions, particularly citrate, to solubilize and enhance phosphorus uptake [108]. Some allelochemicals affect the growth of the plant itself, i.e., autotoxic effect as some derivatives of benzoic and cinnamic acids from the root exudates of cucumber since it inhibits root antioxidant enzymes and leaf photosynthesis, transpiration and stomatal conductance in cucumber [109].

Natural herbicides sound attractive as alternatives for herbicides but their application is still surrounded with much concern since they affect humans and environmental equilibrium. The agricultural community cannot discard the use of synthetic herbicides completely at the present time but their use can be reduced up to a certain extent by utilizing allelopathic potentiality as an alternative weed management strategy for crop production.

7. Future prospects for rationalization of herbicide usage by molecular biology

Rationalization of herbicidal use targets mainly the production of plants which are herbicidal themselves by recruiting allelopathic characters. Allelopathy is considered a genetically influenced factor [91]. Allelopathic characteristics are more likely to evolve in competitive populations such as in wild types [110]. Therefore, it is possible to enhance weed suppressive potential of crop cultivars or to transfer allelopathic characteristics from wild types or

unrelated plants into commercial crop cultivars through conventional plant breeding methods or other genetic recombination strategies. There are two methods for creating herbicidal plant crops that have been suggested; regulation of gene expression related to alleochemicales biosynthesis; or insertion of genes to produce allelochemicals that are not found in the crop [88].

7.1. Gene insertion

The allelopathic phenomenon as mentioned before refers to the ability of some plant species to suppress other species by releasing allelochemicals, which are not toxic to the originating plant but toxic to surrounding vegetation. Breeding allelopathic cultivars by molecular approaches are more complicated than developing an herbicide-resistant crop. Genetic engineering of allelochemicals bases on their overexpression as valuable secondary metabolites in plants [111]. Most secondary metabolites being used as allelochemicals are products of a multi-gene system might which have to be developed and transformed into the specific crop to produce allelochemicals [112, 113].

Gene insertion targets the change of the recent biochemical pathways into another one which is able to produce new allelochemicals through the insertion of transgenes. Although there is great difficulty to satisfy this approach, it represents the promising molecular approaches available for application in the near future. Various reviews in this trend and reference book on molecular biology of weed control [112, 113] were conducted.

7.2. Regulation of gene expression related to allelochemicals

Regulation of gene expression by a biologist first requires accurate identification of the target allelochemical(s), to determine enzymes and the genes encoding them. Accordingly, a specific promoter can be inserted into crop plants to enhance allelochemical production. Allelochemicals are conditionally expressed by biotic and abiotic factors since some metabolites having allelopathic potential might be newly synthesized or highly elevated in rice plants by UV irradiation [114]. For instance, there is a differential response to UV or other environmental stresses among rice cultivars. The phenylpropanoid pathway intermediates of several allelopathic rice cultivars have the highest content of *p*-coumaric acid. The latter is a key reaction in the biosynthesis of a large number of phenolic compounds in higher plants. Phenolic compounds are derived from cinnamic acid by the catalysis of 4-hydroxylase (CA4H) enzyme. The activity of CA4H was measured to determine its response to UV irradiation in rice leaves of different varieties. *Kouketsumochi* showed induction for CA4H activity by UV after 24 h of UV irradiation for 20 min while the rice cultivar AUS 196 showed no response. The increase in CA4H enzyme activity as a required enzyme in conversion of cinammic acid into *p*-coumaric acid suggested a role for CA4H gene in the elevation of the allelopathic function in rice plants [114].

Responsiveness to environmental stresses and plant-plant interaction may be conferred by a specific promoter. A promoter which its induction is responsive to an elicitor can be used to regulate genes that are responsible for coding allelochemicals. The expression of phytoalexins and pathogenesis related genes in plants were reported in response to UV treatment and other

plant defense inducers [115, 116]. UV was found to stimulate phytoalexine production in pepper. The effective motifs response to UV light was determined in tobacco by examining the expression of GUS activity of plants transformed with the constructs of various CASC (*Capsicum annuum* sesqiterpene cyclase) promoters fused into GUS gene [115]. This was followed by UV irradiation of the transgenic plants to assure the induction of the CASC promoters through examining GUS activity of the transgenic plants. The levels of GUS activity for transgenic plants with pBI121-KF1 and pBI121-KF6 were significantly elevated by UV-irradiation and had a two-to-threefold increase approximately over the untreated-transgenic plants. In contrast, GUS expression in the transgenic plants with pBI121-CaMV 35S was not changed by UV, and in the other constructs had only a very small increase [117]. The CASC promoters of both KF-1 and KF-6 were suggested to contain cis-acting elements capable of conferring quantitative expression patterns that were exclusively associated with UV irradiation. The regulation of genes associated with allelopathy could be achieved by developing a specific promoter responsive to plant-weed competition or environmental stresses. The CASC promoters of KF-1 and KF-6 obtained may be specific to UV. Thus, this promoter can be used for the overexpression of specific promoters constructed to allelochemical-producing genes [116]. To regulate the CA4H gene in the phenylpropanoid pathway, specific promoters, the CASC-KF1 and KF6, were fused to CA4H gene. The gene constructs were introduced into the binary plant expression vector pIG121-HMR with reverse primer harbouring *Bam*HI site and forward primer harbouring *Hin*dIII site as illustrated in Figure 4 [118].

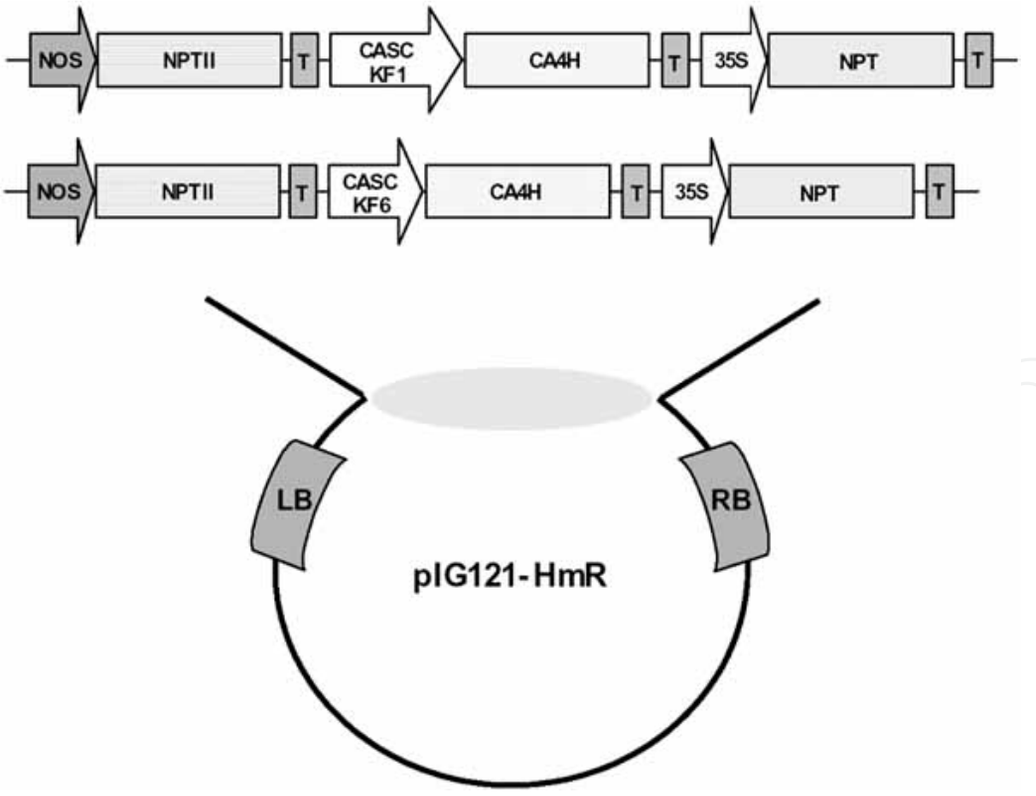

Figure 4. The Gene Cassette with Specific Promoters Responsive to UV Irradiation in pIG121-HmR [117].

8. Conclusion

Herbicides are widely used in agricultural communities on a large scale for eradicating weeds. Herbicides function by affecting different biochemical processes in weeds. Herbicides in low doses act as growth regulators for the main crop but high doses may cause crop damage. However, uncontrolled herbicide use can cause hazardous effects not only upon the main crop but also human health and the surrounding environment [80, 81]. Moreover, heavy doses of herbicides create the problem of herbicide resistance development in weeds. There is an urgent need to identify natural alternatives that can meet the demands of agrosystems without affecting the surrounding environment. Hence, the idea of recruiting the allelopathic phenomenon of some plants in inhibiting the growth of weed vegetation has been investigated. Allelopathy cannot cancel the use of herbicides completely but can minimize it. Allelopathic plant use has limitations in the application because of the potential toxicity. Thus, molecular biology can aid the agricultural community by engineering crops to be herbicides themselves through gene insertion and regulation depending on well-defined allelopathic genes or promoters, respectively. Even with well-characterized allelopathic genes, it might be very difficult to transfer genes into crops.

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